Steady State Performance, Photo-induced Performance Degradation and Their Relation to Transient Hysteresis in Perovskite Solar Cells

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ABSTRACT

Hysteresis in current-voltage curves of perovskite solar cells is a serious concern as it creates confusions about actual cell performance and raises questions on its reliability. Although a lot of effort has been made to understand the origin of hysteresis, knowing whether hysteresis affects the cell performance while they are in practical use (operated constantly at maximum power point) is not yet examined. In the present study, we investigate steady state performance and performance stability of perovskite solar cells (planar architecture with varying perovskite film thickness and TiO₂ mesoscopic structure with different TiO₂ compact layer thickness exhibiting hysteresis of different magnitudes) operating across an external load in relation to hysteresis. The planar cells with larger hysteresis exhibit a steady state current that closely matches the value determined on forward voltage scan. Cyclic photocurrent–dark current measurements on cells with hysteresis of different magnitudes reveal that photo-induced electrical instability (not material degradation), which might be originated from ion migration or photo-induced traps formation, is not related to hysteresis. Performance of the cells is recovered partially or fully, depending on the device structure, on storage in dark. TiO₂ meso-structure cells tend to show complete recovery while the planar cells recover partially.

KEYWORDS

Perovskite solar cells, Hysteresis, Performance stability, Light soaking, Cyclic photo and dark current measurement

1. Introduction

Having emerged as a new alternative photovoltaic technology with huge potential to accomplish better performance through simple solution processes, organometal halide perovskite based solar cells[1-4] have hit the high spots in short time. In the last six years, the progress has been great in terms of achieving power conversion efficiency (PCE), which has increased from 3.8% in a liquid junction device[1] to 20.1% in a solid state structure[5]. One of the interesting facts that could be noticed with progress of the cell performance is evolution of the device structure; the device structure of these solar cells has evolved from mesoscopic structure with an active porous layer (TiO_2) or a passive metal oxide scaffold (Al_2O_3) to planar hetero-junction device without any metal oxide porous structures.⁴ The continuous rise in power conversion efficiency of the cells has drawn enormous attention and the material has become an utmost interest to all in photovoltaic community. Organometal halide perovskite compounds with high absorption coefficient and long range carrier diffusion undergoing minimal recombination show large current density and high open circuit voltage, resulting in high PCE. In general, the last five years have witnessed a race of chasing efficiency without much understanding of the fundamental science behind working of the device. It is doubtless that the device has great potential of achieving high efficiency. However, there are several fundamental issues like durability of the efficiency, wide distribution in performance, difficulties in reproducing the results, hysteresis in current-voltage curves, etc., which require deeper scientific understanding. A thorough understanding would certainly help in finding solutions for stabilizing the high power conversion efficiencies. Amongst all the above problems, hysteresis, which has created doubts about over estimation of cell performance [6-8], has been apparently considered to be major. A good number of studies pertaining to origin of hysteresis have been already reported.

Several mechanisms like ferroelectric polarization[9-13], ion migration[11, 14], deeper trap states in the perovskite[11] and carrier transfer dynamics at interfaces[15-19] have been proposed to be the origin to hysteresis. Unfortunately, there is no consensus about the origin to such hysteretic behavior so far. Although understanding the mechanism of origin to hysteresis is doubtlessly the first step towards finding a solution to this anomalous behavior of perovskite solar cells, knowing how hysteresis can affect the actual cell performance is more appropriate and important. Indeed, it holds more relevance to practical use of the solar cells. The steady state performance of cells operating at a constant voltage (or across an external load) is what matters. Hysteresis may not be a big problem as long as cells with and without hysteresis produce stable and reliable steady state performance across a constant load over time. However, if the phenomena, like ferroelectric polarization, ion migration or interface carrier dynamics, which are being proposed to be responsible for hysteresis, also affect the steady state performance of the cells then hysteresis should be considered equally a big problem. Cells showing larger hysteresis should have greater effects of ferroelectric polarization, ion migration, etc. Hence, it is expected that cells showing greater hysteresis should have poorer stability.

In this study, we compare the steady state performance of the cells showing hysteresis with that of the devices not showing hysteresis. In addition, we check performance stability of the cells in relation to hysteresis. The performance measured with a constant external load put in series across the cells of both planar and meso-structure exhibiting little, moderate and huge hysteresis has been compared. The performance stability checked by cyclic photocurrent and dark current measurements (constant current switched by cyclic on and off of light) reveals that temporary electronic/ionic change in the device, regardless of the existence of hysteresis, is critical for

performance reduction. **Importantly, hysteresis is not related to the problem of performance instability.**

2. Experimental

2.1 Device fabrication

Planar hetero-junction perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells with perovskite films of different thicknesses were fabricated by one-step solution method in dry (relative humidity is almost 0%) atmospheric conditions. Thickness of the perovskite film was controlled by spin-coating the precursor solution (a 40 wt% mixed solution of PbCl_2 (Aldrich) and $\text{CH}_3\text{NH}_3\text{I}$ (synthesized in lab) in N,N-Dimethylformamide in a molar ratio of 1:3 (PbCl_2 : MAI)) at 1500, 3000 and 6000 rpm for 60s following a hold time at 0 rpm for 30 s after dropping the solution on sputtered or spray-pyrolysis TiO_2 compact layer-coated FTO substrates. The perovskite-coated substrates were then heated at 100°C on a hot plate for 45 min for complete formation of crystalline $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. The perovskite films were cooled down to room temperature and then a 12 wt% solution of 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, from Merck) including lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) and tert-butylpyridine (t-BP) as dopant and additive respectively in chlorobenzene was coated at a spinning speed of 4000 rpm for 60s. A planar device free of compact layer was made by spin-coating perovskite solution directly on FTO substrate at 1500 rpm for 60s followed by annealing and spiro-OMeTAD coating at same conditions as followed for other planar devices. The procedure of fabrication for the planar perovskite cell by toluene dripping method is given in supplementary information.

For making TiO₂-mesoporous layer, TiO₂ paste (Solaronix-T/SP) diluted in ethanol (1:3 by weight) and then spin-coated at 500 rpm for 10 s followed by 3000 rpm for 30 s on TiO₂ compact layer-FTO substrates prepared by TiCl₄ dip-coating and spray-pyrolysis method, dried at 120 °C for 5 min and then sintered at 500 °C in a muffle furnace. The 40 wt% precursor solution of perovskite (as given above) was then spin-coated on the TiO₂ mesoporous layer at 2000 rpm for 30 s following a hold at 0 rpm for 60 s. The films were then annealed at 100 °C on hot plate for 45 min for crystallization of CH₃NH₃PbI_{3-x}Cl_x. A spiro-OMeTAD solution of composition as given for planar cells was then coated on the perovskite film at 3000 rpm for 30 s followed by a hold at 0 rpm for 30 s. The Au back contact was vacuum-deposited on spiro-OMeTAD films both in planar and TiO₂-mesoscopic devices by thermal evaporation technique after ageing the spiro-OMeTAD layer overnight.

Spray-pyrolysis TiO₂ compact layers were prepared by spraying diluted solution of titanium diisopropoxide bis (acetylacetonate) solution (75 wt%, Aldrich) in ethanol (100 µl Ti (acac) + 1 ml EtOH) on the cleaned FTO substrates at 450 °C. The compact layers were kept at 450 °C for 45 min on the hot plate and then further annealed at 500 °C in a muffle furnace. Thickness of the CL, as measured from the cross sectional view of scanning electron micrographs, was controlled by volume of the solution used for spraying. TiCl₄ dip-coated TiO₂ CL was made by dipping the FTO substrates in a 100 mM aqueous solution of TiCl₄ (make) at 70 °C for 60 min and then rinsing with water followed by heating at 500 °C.

2.2 Device characterization

Photovoltaic characterization of the devices was done by measuring current on voltage scan in forward (-0.1 V to 1.1 V) and backward (1.1 V to 0 V) directions both under light (100 mW/cm²

AM1.5, 1 sun intensity) provided by a solar simulator (Peccell Technologies PEC-L01) and dark. A Keithley source meter (Model 2400) was used for all electrical measurements. The voltage scan speed used to obtain photocurrent density-voltage (J-V) curves was kept at 200 mV/s. The active area of the device was 0.09 mA/cm². For steady state current measurement, current from the cells was measured for more than 2 minutes either at a bias voltage equal to voltage corresponding to maximum power point (determined from current-voltage (I-V) scan) or with a resistance of 600 ohm put in series to the devices. Performance durability of the cells was checked by cyclic photocurrent and dark current measurement performed on the cells either at bias voltage equal to V_{mpp} or with a series resistance of 600 ohm while the light source was put on (for 3 minutes) and off (for 3 minutes) by an automatic shutter. Each device was subjected to 10 on-off cycles of measurement, which endured for about 1 hour. For checking the effect of light soaking on performance of the cells, I-V scan on the devices was made before and after keeping the cells at open circuit condition under 1 sun illumination for 1 hour. The cells were stored in dark in a desiccator for different time durations after cyclic on/off and light soaking measurements for checking recovery of the cell performance. In order to determine thickness of different layers in the cells, cross-sectional scanning electron micrographs of the cells was taken with a scanning electron microscope (SEM) (SU8000, HITACHI). X-ray diffraction analysis of perovskite was done by taking XRD patterns (Bruker Model D8 Discover) of perovskite on complete device before and after cyclic photocurrent/dark current measurements. All the electrical measurements were taken on non-encapsulated cells in ambient atmosphere (30-40% humidity) at room temperature.

3. Results and discussion

3.1 Hysteresis, steady state performance and performance stability of planar

heterojunction perovskite solar cells

Figure 1 (a) shows current-voltage (J-V) curves of planar hetero-junction cells with perovskite films of different thicknesses (500-600 nm, 300-400 nm, 100-200 nm) prepared by spin-coating the perovskite precursor solution at different speeds (1500 rpm-60s, 3000 rpm-60s, 6000 rpm-60s) on TiO₂ compact layer (100-120 nm) made by spray pyrolysis. Photocurrent density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and PCE values of the devices obtained on both forward (FS) and backward (BS) voltage scan are listed in table 1. The cross sectional scanning electron microscopy (SEM) images of the planar cells with perovskite films of different thicknesses are given in Figure S7. As can be seen in Figure 1 (a), the planar perovskite solar cells exhibited obvious hysteresis. However, the magnitude of hysteresis was found to increase with thickness of the perovskite film. Planar cells with thin perovskite film (100-200 nm) showed almost no hysteresis while the thicker film (500-600 nm) exhibited huge hysteresis. In order to determine the steady state (ss) current density of the cells at a particular voltage of operation and compare this value with the transient values found on voltage scan (forward and backward), current density of the devices was measured constantly for 2 min with an external load of 600 ohm put in series to the devices (Figure 1 b). The voltage of operation (V_{op}) was measured across the cells while they were operating with the load. Although it was desired to operate all the devices at their maximum power point (V_{mpp}) by either selecting suitable loads or setting the external bias voltage equal to V_{mpp} , we avoided such measurements (biasing at V_{mpp} or selecting the exact load for matching V_{op} with V_{mpp}) because of strong effect of bias voltage on cell performance and limitation of the equipment that could automatically tune the load continuously over time to keep the device at V_{mpp} . In order to avoid the effect of bias voltage on cell performance we chose to operate the device with load instead of biasing at V_{mpp} , kept the

load same for all the devices and measured V_{op} for comparing the ss value with the I-V scan current values at $V = V_{op}$. The results showing the influence of bias voltage on cell performance and detailed discussion about the measurement methods adopted for the present study are given in supporting information. The ss current density measured at V_{op} was compared with the current density determined at the voltage (on forward and backward scan) equal to V_{op} (i.e $V_{scan} = V_{op}$). Figure 1 b shows the time course of ss photocurrent density for perovskite films of different thickness and the values of operating voltage (V_{op}), ss current density (J_{ss}) and current density at voltage equal to V_{op} for forward (J_{FS}) and backward (J_{BS}) scan for all the three planar cells are listed in table 2. For the cells showing moderate or little hysteresis (spin-coated at 3000 rpm and 6000 rpm), the J_{ss} was found to fall between J_{FS} and J_{BS} (see Table 2). As the J_{FS} and J_{BS} values in these cells are not widely different (little/ no hysteresis), it was difficult to determine how closely the ss current density matches with either J_{FS} or J_{BS} . However, in the case of thicker perovskite films (large hysteresis), it was very clear and concrete that the ss current matches the values obtained from forward scan (from short circuit to open circuit). This indicates that the cells showing large hysteresis are more vulnerable to over-estimation of the performance by backward voltage scan that always shows higher current at the same voltage.

Although 2 min is long enough for determining the steady state current values, the duration is too short for evaluating performance stability of the cells. In order to check the performance stability, we measured photocurrent density of the cells (not encapsulated) operated across the load (600 ohm) with cyclic on and off of light (1 sun). The time for each on and off cycle was fixed to 3 minutes and all the devices were measured for 10 cycles, enduring almost 1 hour for the complete measurement. Figure 2 (a) shows current density vs. time curves (cyclic on-off of light) of the planar cells with perovskite films of different thickness. It is evident (Fig 2 a) that

current density of cells with thinner perovskite films (spin-coated at 6000 rpm) does not change much while the same for devices with thicker perovskite films (spin-coated 1500 rpm) drops faster with the number of on/off cycles. J_{sc} of the cells with thicker perovskite film (500-600 nm) decreases from 9.5 mA/cm² in the first light cycle (light on) to 3.0 mA/cm² in the 10th light cycle while that for a cell with thinner perovskite film decreases from 10.9 to 10.0 mA/cm² after completion of 10th cycle. Perovskite films of intermediate thickness (spin-coated at 3000 rpm) exhibited drop in performance at an intermediate rate. The same trend of performance degradation, showing faster drop for thicker perovskite films, was also observed for devices with TiO₂ CL made by sputter deposition (Figure S5), the cells free of CL (and S6) and the cells made by toluene dripping method (Figure S6). In order to check whether this performance degradation reaches a stable minimum after sometime, we measured current density of the devices continuously for 1 h. The photocurrent measured with continuous exposure of light (1 sun) for 1 hour also shows constant degradation of performance for all the three structures (Fig. 2 b).

Hysteresis increased and performance stability decreased with thickness of the perovskite film in the planar perovskite solar cells (Fig. 2), indicating that hysteresis may be directly related to such performance instability of the cells. In order to confirm this relation, we compared the performance of a set of cells with perovskite films of different thicknesses but showing similar hysteresis. Here, the planar perovskite cells with thicker TiO₂ CL (~ 200 nm) and perovskite films of different thickness (spin-coated at 1500, 3000 and 6000 rpm) showed substantially lower J_{sc} (believed to be limited by the thicker CL) and similar hysteresis without much dependence on the perovskite film thickness. Despite of insignificant difference in hysteresis (Figure 3 a), all these cells demonstrated same decreasing trend of performance stability with thickness of perovskite (Fig. 3 b), as was observed for cells with thinner TiO₂ CL (Fig. 2 a) showing

hysteresis increasing with perovskite thickness. This confirms that the performance instability is not directly related to hysteresis; both must have different mechanisms (discussed later). However, hysteresis and performance stability are independently affected by thickness of the perovskite film.

It was found that the performance not only degraded on cyclic or continuous photocurrent measurement but also degraded when the cells were kept under light at open circuit (no current collected from the devices). This, indeed, evidenced that the cell performance decreases with light soaking, regardless of close or open circuit condition of the device. Figure 4 shows J-V curves of two cells, one with thicker (1500 rpm) and the other with thinner perovskite film (6000 rpm), measured before and after soaking the cells under light (1 sun) at open circuit condition for 1 hour. In the case of thicker and hysteretic perovskite film, J_{sc} decreased from 18.2 to 6.1 mA/cm^2 and V_{oc} dropped down from 0.93 V to 0.60 V (Fig 4 a). PCE of the cell, calculated from backward scan, decreased from 10.6% to 1.2%. In comparison, the cell with thinner perovskite film demonstrated lesser drop in the performance; J_{sc} changed from 16.8 to 13.5 mA/cm^2 , V_{oc} decreased from 0.833 to 0.778 V (Fig 4 b), and PCE decreased from 8.0% to 5.8%.

It was surprising but interesting to find that even though the current density in case of thicker perovskite films decreased drastically after the cyclic light on/off measurements (Fig. 2) or continuous light soaking (Fig 4 a), color of perovskite in the samples remained unchanged. Figure S7 (SI) shows photographs and X-ray diffraction patterns of a set of samples before and after the cyclic measurements. The X-ray diffraction analysis of the cells before and after cyclic measurements showed no change in the perovskite peaks, confirming that no degradation of perovskite occurs during the measurement. This fact was also evident from partial or complete recovery of the performance on relaxation of the devices in dark after the cyclic or light soaking

measurements. Some cells showed better recovery than others. For instance, a cell with thicker perovskite film (1500 rpm) (Fig. 5 a) showed more than 50% recovery in J_{sc} (from 11.1 to 12.8 mA/cm^2 while the initial J_{sc} was 13.8 mA/cm^2) while a device of same structure exhibited almost no recovery in J_{sc} (from 9.4 to 9.6 mA/cm^2 while initial J_{sc} was 15.1 mA/cm^2) after storing both the cells in dark for 1 hour (Fig. 5 b). Nevertheless, both the cells showed almost 100% recovery in V_{oc} . It is apparent that the recovery process strongly depends on the history of electrical conditions applied to the samples and time of storage in dark. We observed that some of the devices with thinner perovskite film (6000 rpm), which had not recovered after storing in dark for 1 hour, showed complete recovery after storing in dark for two weeks (Fig. S8 a). However, none of the planar perovskite cells with thicker perovskite film (1500 rpm) recovered completely after 2 weeks (Fig. S8 b). Hence, it was difficult to correlate this process of recovery to structure of the planar cells as the devices of same structure also showed recovery to different extents, which might be influenced by the history of electrical conditions applied before the measurement. However, this process of recovery was found to be more consistent in TiO_2 mesoscopic perovskite cells, which is discussed in the following section.

3.2 Hysteresis, steady state performance and performance stability of TiO_2 meso-structure perovskite solar cells

In a similar manner as was done for planar cells, the steady state and cyclic photocurrent-dark current measurements were taken on three TiO_2 meso-structure perovskite solar cells that differ in thickness of TiO_2 compact layer used. In one case, the compact layer (CL) was prepared by TiCl_4 dip-coating method, which formed a very thin TiO_2 layer, almost invisible with SEM (Fig. S9 a). In the other two cases, the TiO_2 CLs were prepared by spray pyrolysis method but they differ in thickness; 50-60 nm (Fig. S9 b) and 150-180 nm (Fig. S9 c). The cells with either the

TiCl_4 dip-coated or thinner spray pyrolysis TiO_2 CL (50-60 nm) showed almost no hysteresis while that with thicker CL (150-180 nm) exhibited slight hysteresis (Fig. 7 a). The steady state current density of the three cells apparently matched with the values obtained at the voltage equal to V_{op} on both forward and backward voltage scans (Fig 6 b, Table 3). The cell showing slight hysteresis (thicker TiO_2 CL) exhibited ss current density of 16 mA/cm^2 while the values from I-V scan at the same voltage (0.55 V) were 15.9 and 16.3 mA/cm^2 for FS and BS respectively (Table 3). There was obviously no ambiguity about the performance in these cells as they showed almost no hysteresis. However, a continuous drop in the J_{sc} of the cells with time of measurement was observed. J_{sc} of these cells started decreasing immediately after the peak value is attained (within few seconds) and kept on going down as long as the light is on. The measurement taken under cyclic on/off of the light (Fig. 6 c) shows that the current density decreases with time till the light is on (each light cycle). As can be seen in the Fig. 6 c, current at the start of each light cycle is higher than the current measured at the end of the previous light cycle. This indicates that the drop in current density is caused by light, which was also evident from light soaking measurement at open circuit (Fig. 7). However, unlike the planar structure perovskite cells, the TiO_2 meso-structure devices showed almost complete recovery in most of the cases. Figure 7 shows the J-V curves of all three meso-structure cells before, immediately after and 1 hour after (stored in dark) the cyclic photocurrent and dark current (a, b, c) and light soaking at open circuit for 1 hour (d, e, f) measurements. Such recovery of the cell performance confirms that perovskite is not degraded during the measurement. Cyclic photocurrent and dark current measurement and light soaking (1 h) with an ultra-violet cut off filter (absorbing light below 500 nm) also confirms no photodegradation of perovskite by TiO_2 mesoporous layer (Figure S 10).

All the results both from planar and TiO_2 meso-structure cells indicate that the perovskite devices definitely undergo some electrical change under light without degradation of perovskite and thereby, the performance decreases continuously with time of measurement and recovers on storage in dark. Such deterioration in performance is certainly different from the material (perovskite) degradation taking place due to either moisture[20, 21] or oxygen[22]. It is evident that this reversible electrical change is not necessarily affected directly by hysteresis. It has been reported recently that hysteresis in perovskite solar cells emerges due to unbalanced carrier extraction in the device [23, 24]. As evident from the results of local potential distribution in different layers of the device [24], electrons are extracted at a faster rate than holes, ending up in accumulation of holes in perovskite. We strongly believe that such unbalanced carrier extraction, as a transient phenomenon, causes hysteresis on the I-V scan. However, performance instability of the cells observed on cyclic or light soaking measurement may not be due to accumulation of holes as it does not explain continuous degradation of performance under illumination at open circuit. On the other hand, migration of ions [14, 25, 26] and defects (vacancies) [27, 28] to heterojunction interfaces can cause electrical change (localization in charge distribution, etc.) in the junction structure without degradation in the perovskite absorber. Such change can develop a built-in field against the active photovoltage of the cells and can also lead to transient hysteresis. However, regardless of whether hysteresis accompanies, such electrical change, influenced by the structure of interfaces, must be responsible for continuous drop in the steady state cell performance of the perovskite device as studied here. The internal electric field of the device causes ions or vacancies to move near to the interfaces/contacts, resulting in slowing down the carrier extraction. Such ionic transport is enhanced with increase in thickness of perovskite film because of increased mass of ions/defects in the bulk of perovskite. Therefore, the performance

drops faster in planar devices with thicker perovskite film in comparison to those with thinner films. Annihilation or redistribution of these ions/defects is believed to be faster in thinner perovskite films and therefore, perovskite solar cells using TiO_2 mesoporous scaffold show better recovery in performance when stored in dark. It has been recently reported that reversible photo-induced trap states are generated in the perovskite under light and these trap states are responsible for performance degradation[29]. Therefore, a deeper and more systematic investigation is required to understand whether ion migration or photo-induced traps generation is causing continuous degradation in performance. Further investigation is required to understand more about the process of annihilation of such ionic/electronic change in the device.

3.3 Proposed model to explain hysteresis

Based on the results of planar cells with different perovskite and TiO_2 compact layer thickness, we propose a model that can explain hysteresis more consistently. A hysteretic J-V curve implies that there is a clear difference in carrier collection at a given voltage during the forward and backward scan. It is known that at any given voltage backward scan always gives higher current than the forward scan, confirming that carrier collection is always more efficient during the backward scan. In general, carrier collection in the device depends on carrier generation, separation, its transport in the bulk of the layers and transfer at different interfaces in the device. As carrier generation and separation are considered fast processes and depend only on illumination (not on the voltage scan) any difference in collection and thus, in the photocurrent, must be influenced by transport and/or transfer at the interfaces. If these two processes are slow enough to be comparable with the applied voltage scan speed then carrier collection is going to be obviously affected by the voltage scan. It is known that hysteretic behavior depends on the speed of voltage scan and the current measured on a fast scan of voltage is actually a transient

current[9]. This transient current measured on forward scan is smaller than steady state current while the same measured on backward scan is larger than steady state current, resulting in hysteresis on a fast voltage scan.

In a simple planar structure (FTO/ECL/Perovskite/HTM), transport of carrier (electron) depends on bulk property of perovskite while its extraction depends on the properties of the electron collecting layer (ECL). Figure 8 (a) shows the schematic of a planar cell illustrating transport and transfer rate of electrons. Figure 8 b presents a simple analogy (two interconnected water tanks) to the carrier transport, transfer and collection process. Forward scan (from 0 to OCV) and backward scan (from OCV to 0V) in the device can be directly related to opening and closing of the valves (V1 and V2) respectively.

Let's suppose that the rate of transport of electron in the bulk of perovskite and transfer through the ECL (usually TiO_2 CL) are Q_b and Q_t respectively. We assume that Q_b and Q_t are functions of applied voltage. If Q_b and Q_t change at different rates with change in applied voltage (analogy- valve 1 and valve 2 are opened/closed at different rates) then there will emerge a transient state ($Q_b \neq Q_t$), which will take time to reach a steady state ($Q_b = Q_t$). Since collection happens at the interface, the transient current will essentially depend on Q_t . Now, there can be three cases (as illustrated in Fig. 8 c), depending on the properties/characteristics of the perovskite layer and ECL. In case 1, Q_t changes faster than Q_b with voltage ($dQ_t/dV \gg dQ_b/dV$) and transient current (Q_{trans}) measured during forward scan (valves closing) will be less than Q_{ss} and on backward scan (valves opening), Q_{trans} will be higher than Q_{ss} . This is the usual case of hysteresis. With increase in thickness of perovskite film, dQ_b/dV becomes further low (compared to dQ_t/dV), which can be due to several possible reasons such as higher volume fraction of grain boundaries, reduced internal field, more available mobile ions, more photo-induced trap states,

etc in the thicker films. As a result, the difference between Q_{ss} and Q_{trans} becomes higher for thicker perovskite film, which is reflected as greater hysteresis in case of thicker films.

For thicker TiO_2 CL, where collection is limited by the CL, Q_t must be too low and dQ_t/dV is significantly slow to reflect the effect of perovskite thickness and hence, we see similar hysteresis for all three different thicknesses of perovskite film. In case 2, where Q_b and Q_t change at almost same rates ($dQ_b/dV=dQ_t/dV$) with voltage (valve 1 and valve 2 are opened/closed at same rates) the ss is achieved within no time and no hysteresis is observed as the result. This represents the case of TiO_2 mesostructure cells and planar cells with PCBM and other organic ECL that show no or negligible hysteresis [16, 17]. In case 3, where $dQ_t/dV \ll dQ_b/dV$, the Q_{trans} during forward and backward scan will be respectively higher and lower than Q_{ss} . In this case, hysteresis is reversed, showing higher current during forward scan. Although we never observe such reverse hysteresis in the perovskite solar cells, it is another possibility which can be realized with suitable selection of the ECL.

4 Conclusions

Hysteresis increases with thickness of perovskite film in planar structure perovskite solar cells. The cells with thick perovskite films (400-600 nm) show large hysteresis while the devices with thin perovskite film (100-200 nm) show slight or no hysteresis at all. The cells exhibiting large hysteresis yield steady state current density that matches closely with that measured on the forward voltage scan, indicating that the performance of such devices can be overestimated on backward scan measurement. Cyclic photocurrent and dark current measurement of the cells with perovskite films of different thickness reveals that performance degradation rate increases with thickness of perovskite film. However, this performance degradation is not directly related to hysteresis. Planar cells with thicker CL (~200 nm TiO_2 CL) showing same hysteresis,

regardless of thickness of perovskite, demonstrated same decreasing trend of performance stability with increasing thickness of perovskite. TiO_2 meso-structure devices exhibiting no hysteresis also showed continuous drop in performance under light, which also supports the fact that performance instability is not directly linked to hysteresis. It is confirmed that such reduction in performance by cyclic photocurrent and dark current measurement or continuous light soaking at open circuit is not due to degradation of perovskite but because of some temporary electrical change taking place in the device and the devices show revival of performance when stored in dark. However, recovery in performance depends on structure of the cell. Some planar devices show partial recovery while almost all TiO_2 meso-structure devices demonstrated nearly complete recovery after storing in dark because no material degradation involved. Hence, hysteresis is not a critical factor for cell durability. It only creates ambiguity about the actual performance, which we found to match better with the forward scan values for cells showing huge hysteresis. On the other hand, the temporary change (electronic or ionic) taking place in bulk of perovskite under illumination is rather a bigger problem. This change prevents carrier extraction and as a result, performance degrades continuously. Hysteresis and performance instability are fundamentally two different outcomes, the former being related to carrier dynamics in the bulk and at interfaces while the latter is apparently due to some change taking place in bulk of perovskite when the cells are under light regardless of open or close circuit. Further investigation is required to understand this reversible change (ionic/electronic) better.

ASSOCIATED CONTENT

Supporting Information

Scanning Electron Micrographs (cross sectional view) of planar architecture and TiO₂ mesostructure perovskite solar cells, Photographs and XRD of planar cells taken before and after cyclic photocurrent and dark current measurement.

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List of tables

Table 1 J_{sc} , V_{oc} , FF and PCE values obtained from both forward (FS) and backward (BS) I-V scans performed on planar perovskite solar cells with perovskite films of different thicknesses prepared by spin-coating the perovskite solution at different speeds (The corresponding J-V curves are given in Fig. 1).

spin-coating speed	Perovskite film thickness	J_{sc} (mA/cm ²)		V_{oc} (V)		FF		PCE (%)	
		FS	BS	FS	BS	FS	BS	FS	BS
1500 rpm	500-600	15.5	15.7	0.965	1.0	0.34	0.63	5.1	9.9
3000 rpm	300-400	15.1	14.8	0.905	0.935	0.42	0.57	5.8	7.9
6000 rpm	100-200	16.4	15.4	0.877	0.877	0.54	0.61	7.7	8.2

Table 2 Steady state current density (J_{ss}) and current density measured on forward (J_{FS}) and backward (J_{BS}) voltage scan at a voltage equal the voltage of operation (V_{op}) measured across the planar perovskite cells with varying thickness of perovskite film while they were operating across an external load of 600 ohm.

Perovskite film thickness (nm)	Operating Voltage (measured with 600 ohm load)	Steady state current (mA/cm ²) (measured with 600 ohm)	Current density measured from I-V scan at voltage equal to operating voltage	
			J_{FS} (mA/cm ²)	J_{BS} (mA/cm ²)
500-600	0.52	9.5	9.5	14.3
300-400	0.51	10.8	10.6	11.0
100-200	0.68	11.1	10.5	11.2

Table 3 Steady state current density (J_{ss}) and current density measured on forward (J_{FS}) and backward (J_{BS}) voltage scan at a voltage equal the voltage of operation (V_{op}) measured across the TiO_2 meso-structure perovskite solar cells with different compact layers while they were operating across an external load of 600 ohm.

TiO_2 Compact layer	Operating Voltage (measured with 600 ohm load)	Steady state current (measured with 600 ohm)	Current density measured from I-V scan at voltage equal to operating voltage	
	V_{op} (V)	J_{ss} (mA/cm ²)	J_{FS} (mA/cm ²)	J_{BS} (mA/cm ²)
$TiCl_4$ dip-coated	0.59	11.8	10.5	10.7
Spray-pyrolysis (50-60 nm)	0.63	12.1	12.5	12.6
Spray-pyrolysis(150-180 nm)	0.60	11.3	10.5	11.7

Figures

(a)

(b)

Figure 1

(a)

(b)

Figure 2

(a)

(b)

Figure 3

(a)

(b).

Figure 4

Figure 5

Figure 6

Figure 7

<p>Case 1 $dQ_t/dV > dQ_b/dV$</p> <p>(i) From 0 to 1 V (Foward scan) $Q_{trans} (= Q_t) < Q_{ss}$</p> <p>(ii) From 1 to 0 V (Backward scan) $Q_{trans} (=Q_t) > Q_{ss}$</p> <p>Hysteresis</p>	<p>Case 2 $dQ_t/dV = dQ_b/dV$</p> <p>(i) From 0 to 1 V (Foward scan) $Q_t = Q_b = Q_{ss}$</p> <p>(ii) From 1 to 0 V (Backward scan) $Q_t = Q_b = Q_{ss}$</p> <p>No hysteresis</p>	<p>Case 3 $dQ_t/dV < dQ_b/dV$</p> <p>(i) From 0 to 1 V (Foward scan) $Q_{trans} (= Q_t) > Q_{ss}$</p> <p>(ii) From 1 to 0 V (Backward scan) $Q_{trans} (=Q_t) < Q_{ss}$</p> <p>Reverse hysteresis</p>
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(c)

Figure 8

Figure captions

Figure 1 (a) Forward scan (FS-dash lines) and backward scan (BS-solid lines) J-V curves, (b) steady state current density (measured with an external load of 600 ohm) of planar perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells made of perovskite films of three different thicknesses, 500-600 nm, 300-400 nm, 100-200 nm, made by spin-coating the perovskite solution at 1500, 3000, and 6000 rpm for 60s respectively on TiO_2 compact layer (~100-120 nm) made by spray pyrolysis.

Figure 2 (a) cyclic photocurrent (3 min) and dark current (3 min) (measured with the external load of 600 ohm) (b) continuous photocurrent (measured with the external load of 600 ohm for 1 h) of planar perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells made of perovskite films of three different thicknesses, 500-600 nm, 300-400 nm, 100-200 nm, made by spin-coating the perovskite solution at 1500, 3000, and 6000 rpm for 60s respectively on TiO_2 compact layer (~100-120 nm) made by spray pyrolysis.

Figure 3 (a) J-V curves and (b) Current density-time curves (cyclic photocurrent and dark current measurement) of planar cells with perovskite films of different thickness made by spin-coating at 1500, 3000 and 6000 rpm on thick TiO_2 CL (>200 nm) prepared on FTO substrate. Each light and dark cycle was of 3 minutes.

Figure 4 J-V curves measured before and after light soaking (1 sun) of planar perovskite solar cells with (a) thicker (1500 rpm) and (b) thinner (6000 rpm) perovskite films made on sputtered TiO_2 CL.

Figure 5 J-V curves of planar perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) solar cells with thicker perovskite film (spin-coated at 1500 rpm on sputtered TiO_2 CL), measured before, immediately after and 1

hour after (stored in dark) the cyclic photocurrent and dark current measurement across a load of 600 ohm, under cyclic on (3 min) and off (3 min) of light (1 sun).

Figure 6 (a) Forward scan (FS-dash lines) and backward scan (BS-solid lines) J-V curves, (b) steady state current density (measured with an external load of 600 ohm) and (c) cyclic photocurrent (3 min) and dark current (3 min) (measured with the external load of 600 ohm) of TiO₂ meso-structure perovskite (CH₃NH₃PbI_{3-x}Cl_x) solar cells with TiO₂ compact layer prepared by TiCl₄ treatment and spray pyrolysis (50-60 nm and 150-180 nm).

Figure 7 J-V curves of TiO₂ meso-structure perovskite solar cells with TiCl₄ dip-coated (a and d), 50-60 nm (b and e) and 150-180 nm (c and f) spray-pyrolysis TiO₂ CLs, measured before, immediately after and after storing in dark for 1 h following the cyclic on/off measurement (a, b, c) and light soaking (at open circuit for 1 h) measurement (d, e, f).

Figure 8 (a) Schematic of a planar architecture perovskite solar cell showing electron transport in bulk of perovskite and transfer at the electron collecting layer (ECL), (b) Schematic of Two-tank analogy for the carrier transport and transfer taking place in perovskite solar cells, (c) Illustration of three possible cases of hysteresis, based on the electrical properties of the perovskite and ECL.